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Published*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.***(54) Title:** A PROCESS FOR THE PRODUCTION OF PAPER**(57) Abstract**

The invention relates to a process for the production of paper from a suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a drainage and retention aid comprising a cationic or amphoteric polysaccharide, forming and dewatering the suspension on a wire, wherein the cationic polysaccharide has a hydrophobic group. The invention further relates to a process for the production of paper from a suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a dry strength agent comprising a cationic or amphoteric polysaccharide, forming and dewatering the suspension on a wire, wherein the polysaccharide has a hydrophobic group.

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A process for the production of paper

This invention relates to papermaking and more specifically to a process for the production of paper in which a cationic or amphoteric polysaccharide containing hydrophobic substitution is added to a papermaking stock. The process provides 5 improved drainage and retention as well as improved dry strength of the paper produced by the process.

Background

In the papermaking art, an aqueous suspension containing cellulosic fibres, and optional fillers and additives, referred to as stock, is fed into a headbox which ejects the 10 stock onto a forming wire. Water is drained from the stock through the forming wire so that a wet web of paper is formed on the wire, and the web is further dewatered and dried in the drying section of the paper machine. Water obtained by dewatering the stock, referred to as white water, which usually contains fine particles, e.g. fine fibres, fillers and additives, is usually recirculated in the papermaking process. Drainage and retention aids 15 are conventionally introduced into the stock in order to facilitate drainage and increase adsorption of fine particles onto the cellulosic fibres so that they are retained with the fibres on the wire. Cationic and amphoteric polysaccharides like cationic starch and cationic guar gums are widely used as drainage and retention aids. The polysaccharides can be used alone or in combination with other polymers and/or with anionic micro- 20 particulate materials such as, for example, anionic inorganic particles like colloidal silica. Cationic and amphoteric polysaccharides are also widely used as dry strength agents which are introduced into the stock to produce paper with improved dry strength.

Cationic polysaccharides are usually prepared by the reaction of a polysaccharide with a quaternising agent, e.g. 3-chloro-2-hydroxypropyl trimethylammonium 25 chloride, 2,3-epoxypropyl trimethyl ammonium chloride, and 2-chloroethyl trimethyl ammonium chloride.

U.S. Patent Nos. 4,388,150; 4,755,259; 4,961,825; 5,127,994; 5,643,414; 5,447,604; 5,277,764; 5,607,552; 5,603,805; and 5,858,174; and European Patent No. 500,770 disclose the use of cationic and amphoteric polysaccharides and anionic inorganic 30 particles as stock additives in papermaking. These additives are among the most efficient drainage and retention aids now in use.

The Invention

According to the present invention it has been found that improved drainage and retention can be obtained in the manufacture of paper by using a drainage and retention 35 aid comprising a cationic and/or amphoteric polysaccharide containing a hydrophobic group substituent, i.e. a hydrophobe. It has also been found that the cationic and/or

amphoteric polysaccharide containing a hydrophobic group provides improved dry strength of the paper. More specifically, the present invention relates to a process for the production of paper from a suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a drainage and retention aid comprising a cationic or amphoteric polysaccharide, forming and dewatering the suspension on a wire, wherein the polysaccharide has a hydrophobic group. The invention further relates to a process for the production of paper from a suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a dry strength agent comprising a cationic or amphoteric polysaccharide, forming and dewatering the suspension on a wire, wherein the polysaccharide has a hydrophobic group. In a preferred aspect of the invention, the process further comprises forming and dewatering the suspension on a wire to obtain a wet web containing cellulosic fibres, or paper, and white water, recirculating the white water and optionally introducing fresh water to form a suspension containing cellulosic fibres, and optional fillers, to be dewatered to form paper, wherein the amount of fresh water introduced is less than 30 tons per ton of dry paper produced. The invention thus relates to a process as further defined in the claims.

The process of this invention results in improved drainage and/or retention and hereby the present process makes it possible to increase the speed of the paper machine and to use lower a dosage of additive to give a corresponding drainage and retention effect, thereby leading to an improved papermaking process and economic benefits. Further benefits observed with the present invention include improved dry strength of the paper produced using the polysaccharide having a hydrophobic group. Hereby it is possible to use lower a dosage of dry strength agent to give a corresponding paper dry strength effect. The process of this invention is suitably used for the treatment of cellulosic suspensions in closed mills wherein the white water is repeatedly recycled with the introduction of only low amounts of fresh water. The process is further suitably applied to papermaking processes using cellulosic suspensions having high salt contents, and thus having high conductivity levels, for example processes with extensive white water recycling and limited fresh water supply and/or processes using fresh water having high salt contents.

The polysaccharide according to this invention can be selected from any polysaccharide known in the art including, for example, starches, guar gums, celluloses, chitins, chitosans, glycans, galactans, glucans, xanthan gums, pectins, mannans, dextrans, preferably starches and guar gums. Examples of suitable starches include potato, corn, wheat, tapioca, rice, waxy maize, etc. Suitably the cationic polysaccharide is water-dispersable or, preferably, water-soluble. In a preferred embodiment of this invention, the polysaccharide is capable of functioning as a drainage and retention aid (agent). The

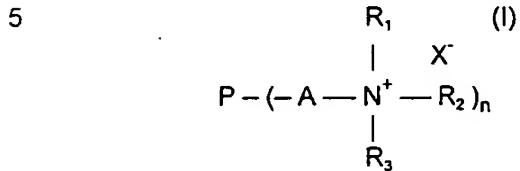
term "drainage and retention aid", as used herein, refers to one or more components (aids, agents, or additives) which, when being added to a stock, give better drainage and/or retention than is obtained when not adding the said one or more components. In another preferred embodiment of this invention, the polysaccharide is capable of 5 functioning as a dry strength agent. The term "dry strength agent", as used herein, refers to at least one component (aid, agent or additive) which, when being added to a stock, give better dry strength of the paper produced than is obtained when not adding the said component.

The polysaccharide is a hydrophobe substituted, cationic or amphoteric 10 polysaccharide, i.e. a polysaccharide having one or more hydrophobic groups and one or more cationic groups, the cationic groups suitably being tertiary amino groups or, preferably, quaternary ammonium groups. The polysaccharide may also contain one or more anionic groups which can be, for example, phosphate, phosphonate, sulphate, sulphonate or carboxylic acid groups and they are preferably phosphate groups. If present, 15 the anionic groups can be native or introduced by means of chemical treatment in conventional manner; native potato starch contains a substantial amount of covalently bound phosphate monoester groups. In amphoteric polysaccharides, cationic groups are preferably present in a predominant amount.

The hydrophobic group of the polysaccharide can be attached to a heteroatom 20 like oxygen present in the polysaccharide. Preferably, the hydrophobic group is attached to a heteroatom, e.g. nitrogen or oxygen, the heteroatom optionally being charged, for example when it is a nitrogen, or a group comprising such a heteroatom, e.g., amide, ester or ether, which, in turn, can be attached to the polysaccharide backbone (main chain), for example via a chain of atoms. The hydrophobic group has at least 2, usually at least 3, 25 suitably at least 4 and preferably at least 6 carbon atoms; and usually up to about 20, suitably up to 14 and preferably up to 12 carbon atoms. The hydrophobic group can be selected from aromatic (aryl) groups, aliphatic hydrocarbon groups, and mixtures of such groups. Examples of suitable hydrophobic aliphatic groups include linear, branched and cyclic alkyl groups like ethyl; propyl, e.g. n-propyl and iso-propyl; butyl, e.g. n-butyl, iso-butyl and t-butyl; pentyl, e.g. n-pentyl, neo-pentyl and iso-pentyl; hexyl, e.g. n-hexyl and cyclohexyl; octyl, e.g. n-octyl; decyl, e.g. n-decyl; and dodecyl, e.g. n-dodecyl; and tetradecyl. Examples of suitable aromatic groups and groups comprising an aromatic group 30 include aryl and aralkyl groups, e.g. phenyl, phenylene, naphthyl, phenylene, xylylene, benzyl and phenylethyl; nitrogen-containing aromatic (aryl) groups, e.g. pyridinium and quinolinium, as well as derivatives of these groups where one or more substituents 35

attached to said aromatic groups can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms.

Particularly suitable polysaccharides according to the invention include those comprising the general structural formula (I):



- wherein P is a residue of a polysaccharide; A is a group attaching N to the polysaccharide residue, suitably a chain of atoms comprising C and H atoms, and optionally O and/or N atoms, usually an alkylene group with from 2 to 18 and suitably 2 to 8 carbon atoms, optionally interrupted or substituted by one or more heteroatoms, e.g. O or N, e.g. an alkyleneoxy group or hydroxy propylene group ($-\text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_2 -$); R₁ and R₂ are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, suitably 1 or 2 carbon atoms; R₃ is a hydrophobic hydrocarbon group containing at least 2 carbon atoms, suitably 4 to 14 and preferably 6 to 12 carbon atoms, the hydrophobic group suitably being as defined above, preferably a group selected from alkyl and aralkyl groups, e.g. benzyl and phenylethyl groups; n is an integer from about 2 to about 300,000, suitably from 5 to 200,000 and preferably from 6 to 125,000 or, alternatively, R₁, R₂ and R₃ together with N form a aromatic group containing from 5 to 12 carbon atoms; and X⁻ is an anionic counterion, usually a halide like chloride.

The hydrophobic group modified cationic or amphoteric polysaccharide can have a

- 25 degree of substitution varying over a wide range; the degree of cationic substitution (DS_c) can be from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, the degree of hydrophobic substitution (DS_H) can be from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, and the degree of anionic substitution (DS_A) can be from 0 to 0,2, suitably from 0 to 0,1, preferably from 0 to 0,05.

- 30 The polysaccharides according to the invention can be prepared by subjecting a polysaccharide to cationic and hydrophobic modification in known manner using one or more agents containing a cationic group and/or a hydrophobic group, for example by reacting the agent with the polysaccharide in the presence of an alkaline substance such as an alkali metal or alkaline earth metal hydroxide. The polysaccharide to be subjected to 35 cationic and hydrophobic modification can be non-ionic, anionic, amphoteric or cationic. Suitable modifying agents include non-ionic agents such as, for example, hydrophobe substituted succinic anhydrides; alkylene oxides, e.g. propylene oxide and butylene oxide;

alkyl halides, e.g. decyl bromide and docecyt bromide; aralkyl halides, e.g. benzyl chloride and benzyl bromide; the reaction products of epichlorohydrin and dialkylamines having at least one substituent comprising a hydrophobic group as defined above, including 3-dialkyl-amino-1,2-epoxypropanes; and cationic agents such as, for example, the reaction product 5 of epichlorohydrin and tertiary amines having at least one substituent comprising a hydrophobic group as defined above, including trialkylamines, alkarylalkylamines, e.g. dimethylbenzylamine; arylamines, e.g. pyridine and quinoline. Suitable cationic agents of this type include 2,3-epoxypropyl trialkylammonium halides and halohydroxypropyl trialkylammonium halides, e.g. N-(3-chloro-2-hydroxypropyl)-N-(hydrophobic alkyl)-N,N-di(lower alkyl)-10 ammonium chloride and N-glycidyl-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride where the hydrophobic alkyl group is as defined above, notably octyl, decyl and dodecyl, and the lower alkyl is methyl or ethyl; and halohydroxypropyl-N,N-dialkyl-N-alkaryl-ammonium halides and N-glycidyl-N-(alkaryl)-N,N-dialkylammonium chloride, e.g. N-(3-chloro-2-hydroxypropyl)-N-(alkaryl)-N,N-di(lower alkyl)ammonium chloride where the alkaryl 15 and lower alkyl groups are as defined above, particularly N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride; and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Generally, when using a non-ionic hydrophobic agent, the polysaccharide is suitably rendered cationic by using any of the cationic agents known in the art before or after the hydrophobic modification. Examples of suitable cationic and/or hydrophobic 20 modifying agents, hydrophobic group modified polysaccharides and methods for their preparation include those described in U.S. Patent Nos. 4,687,519 and 5,463,127; International Patent Application WO 94/24169, European Patent Application No. 189 935; and S.P. Patel, R.G. Patel and V.S. Patel, Starch/Stärke, 41(1989), No. 5, pp. 192-196, the teachings of which are hereby incorporated herein by reference.

25 In a preferred embodiment, the polysaccharide according to the invention is used in conjunction with at least one additional stock additive, in particular for further improving drainage and/or retention, thereby forming a drainage and retention aid comprising two or more components, usually referred to as drainage and retention aids. The term "drainage and retention aids", as used herein, refers to two or more 30 components (aids, agents or additives) which, when being added to a stock, give better drainage and/or retention than is obtained when not adding the components. Examples of suitable stock additives of this type include anionic microparticulate materials, e.g. anionic organic particles and anionic inorganic particles, water-soluble anionic vinyl addition polymers, low molecular weight cationic organic polymers, aluminium 35 compounds, and combinations thereof. In a preferred aspect of this embodiment, the polysaccharide is used in conjunction with an anionic microparticulate material, notably

with anionic inorganic particles. In another preferred aspect of this embodiment, the polysaccharide is used in conjunction with anionic inorganic particles and a low molecular weight cationic organic polymer. In yet another preferred aspect of this embodiment, the polysaccharide is used in conjunction with anionic inorganic particles and an aluminium compound. The anionic microparticulate material according to the invention can be selected from inorganic and organic particles.

Anionic inorganic particles that can be used according to the invention include anionic silica-based particles and clays of the smectite type. It is preferred that the anionic inorganic particles are in the colloidal range of particle size. Anionic silica-based particles, i.e. particles based on SiO_2 or silicic acid, are preferably used and such particles are usually supplied in the form of aqueous colloidal dispersions, so-called sols. Examples of suitable silica-based particles include colloidal silica and different types of polysilicic acid. The silica-based sols can also be modified and contain other elements, e.g. aluminium and/or boron, which can be present in the aqueous phase and/or in the silica-based particles. Suitable silica-based particles of this type include colloidal aluminium-modified silica and aluminium silicates. Mixtures of such suitable silica-based particles can also be used. Drainage and retention aids comprising suitable anionic silica-based particles are disclosed in U.S. Patent Nos. 4,388,150; 4,927,498; 4,954,220; 4,961,825; 4,980,025; 5,127,994; 5,176,891; 5,368,833; 5,447,604; 5,470,435; 5,543,014; 5,571,494; 5,573,674; 5,584,966; 5,603,805; 5,688,482; and 5,707,493; which are hereby incorporated herein by reference.

Anionic silica-based particles suitably have an average particle size below about 50 nm, preferably below about 20 nm and more preferably in the range of from about 1 to about 10 nm. As conventional in silica chemistry, the particle size refers to the average size of the primary particles, which may be aggregated or non-aggregated. The specific surface area of the silica-based particles is suitably above 50 m^2/g and preferably above 100 m^2/g . Generally, the specific surface area can be up to about 1700 m^2/g and preferably up to 1000 m^2/g . The specific surface area can be measured by means of titration with NaOH in known manner, e.g. as described by Sears in Analytical Chemistry 28(1956):12, 1981-1983 and in U.S. Patent No. 5,176,891. The given area thus represents the average specific surface area of the particles.

In a preferred embodiment of the invention, the anionic inorganic particles are silica-based particles having a specific surface area within the range of from 50 to 1000 m^2/g , preferably from 100 to 950 m^2/g . Sols of silica-based particles these types also encompass modified sols like aluminium-containing silica-based sols and boron-containing silica-based sols. Preferably, the silica-based particles are present in a sol having an S-value in the range of from 8 to 45%, preferably from 10 to 30%, containing silica-based

particles with a specific surface area in the range of from 300 to 1000 m²/g, suitably from 500 to 950 m²/g, and preferably from 750 to 950 m²/g, which sols can be modified with aluminium and/or boron as mentioned above. For example, the particles can be surface-modified with aluminium to a degree of from 2 to 25% substitution of silicon atoms. The S-value can be measured and calculated as described by Iler & Dalton in J. Phys. Chem. 60(1956), 955-957. The S-value indicates the degree of aggregate or microgel formation and a lower S-value is indicative of a higher degree of aggregation.

In yet another preferred embodiment of the invention, the silica-based particles are selected from polysilicic acid and modified polysilicic acid having a high specific surface area, suitably above about 1000 m²/g. The specific surface area can be within the range of from 1000 to 1700 m²/g and preferably from 1050 to 1600 m²/g. The sols of modified polysilicic acid can contain other elements, e.g. aluminium and/or boron, which can be present in the aqueous phase and/or in the silica-based particles. In the art, polysilicic acid is also referred to as polymeric silicic acid, polysilicic acid microgel, polysilicate and polysilicate microgel, which are all encompassed by the term polysilicic acid used herein. Aluminium-containing compounds of this type are commonly also referred to as polyaluminosilicate and polyaluminosilicate microgel, which are both encompassed by the terms colloidal aluminium-modified silica and aluminium silicate used herein.

Clays of the smectite type that can be used in the process of the invention are known in the art and include naturally occurring, synthetic and chemically treated materials. Examples of suitable smectite clays include montmorillonite/bentonite, hectorite, beidelite, nontronite and saponite, preferably bentonite and especially such bentonite which after swelling preferably has a surface area of from 400 to 800 m²/g. Suitable clays are disclosed in U.S. Patent Nos. 4,753,710; 5,071,512; and 5,607,552, which are hereby incorporated herein by reference.

Anionic organic particles that can be used according to the invention include highly cross-linked anionic vinyl addition polymers, suitably copolymers comprising an anionic monomer like acrylic acid, methacrylic acid and sulfonated or phosphonated vinyl addition monomers, usually copolymerized with nonionic monomers like (meth)acrylamide, alkyl (meth)acrylates, etc. Useful anionic organic particles also include anionic condensation polymers, e.g. melamine-sulfonic acid sols.

Low molecular weight (hereinafter LMW) cationic organic polymers that can be used according to the invention include those commonly referred to and used as anionic trash catchers (ATC). ATC's are known in the art as neutralizing and/or fixing agents for detrimental anionic substances present in the stock and the use thereof in combination with drainage and retention aids often provide further improved drainage and/or retention. The

LMW cationic organic polymer can be derived from natural or synthetic sources, and preferably it is an LMW synthetic polymer. Suitable organic polymers of this type include LMW highly charged cationic organic polymers such as polyamines, polyamidoamines, polyethyleneimines, homo- and copolymers based on diallyldimethyl ammonium chloride, 5 (meth)acrylamides and (meth)acrylates. The molecular weight of the LMW cationic organic polymer is suitably at least 2,000 and preferably at least 10,000. The upper limit of the molecular weight is usually about 700,000, suitably about 500,000 and preferably about 200,000.

Aluminium compounds that can be used according to this invention include alum, 10 aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium chlorides, polyaluminium sulphates, polyaluminium compounds containing both chloride and sulphate ions, polyaluminium silicate-sulphates, and mixtures thereof. The polyaluminium compounds may also contain other anions than chloride ions, for example anions from sulfuric acid, phosphoric acid, organic acids such as citric acid and 15 oxalic acid.

The components of drainage and retention aids according to the invention can be added to the stock in conventional manner and in any order. When using an anionic microparticulate material, it is preferred to add the hydrophobe substituted, cationic or amphoteric polysaccharide to the stock before adding the microparticulate material, even 20 if the opposite order of addition may be used. It is further preferred to add the polysaccharide before a shear stage, which can be selected from pumping, mixing, cleaning, etc., and to add the anionic particles after that shear stage. When using an LMW cationic organic polymer and/or an aluminium compound, such components are preferably introduced into the stock prior to introducing the polysaccharide and anionic 25 microparticulate material, if used. Alternatively, the LMW cationic organic polymer and polysaccharide can be introduced into the stock essentially simultaneously, either separately or in admixture, e.g. as disclosed in U.S. Patent No. 5,858,174, which is hereby incorporated herein by reference.

The dry strength agent and drainage and retention aid(s) according to the 30 invention are added into the stock to be dewatered in amounts which can vary within wide limits depending on, inter alia, type and number of components, type of furnish, filler content, type of filler, point of addition, salt content, etc. Generally the component(s) are added in an amount that give better paper dry strength and/or drainage and/or retention than is obtained when not adding the component(s). The hydrophobe substituted, cationic 35 or amphoteric polysaccharide is usually added in an amount of at least 0,01%, often at least 0,1% by weight, based on dry stock substance, and the upper limit is usually 10% and

suitably 2% by weight. When using an anionic microparticulate material, it is usually added in an amount of at least 0.001% by weight, often at least 0.005% by weight, based on dry substance of the stock, and the upper limit is usually 1.0% and suitably 0.6% by weight. When using anionic silica-based particles, the total amount added is suitably within the 5 range of from 0.005 to 0.5% by weight, calculated as SiO₂ and based on dry stock substance, preferably within the range of from 0.01 to 0.2% by weight. When using an LMW cationic organic polymer in the process, it can be added in an amount of at least 0.05%, based on dry substance of the stock to be dewatered. Suitably, the amount is in the range of from 0.07 to 0.5%, preferably in the range from 0.1 to 0.35%. When using an 10 aluminium compound in the process, the total amount introduced into the stock to be dewatered is dependent on the type of aluminium compound used and on other effects desired from it. It is for instance well known in the art to utilise aluminium compounds as precipitants for rosin-based sizing agents. The total amount added is usually at least 0.05%, calculated as Al₂O₃ and based on dry stock substance. Suitably the amount is in the 15 range of from 0.5 to 3.0%, preferably in the range from 0.1 to 2.0%.

The process of the invention is preferably used in the manufacture of paper from a suspension containing cellulosic fibers, and optional fillers, having a high conductivity. Usually, the conductivity of the stock that is dewatered on the wire is at least 0.75 mS/cm, suitably at least 2.0 mS/cm, preferably at least 3.5 mS/cm. Very good drainage and 20 retention results have been observed at conductivity levels above 5.0 mS/cm and even above 7.5 mS/cm. Conductivity can be measured by standard equipment such as, for example a WTW LF 539 instrument supplied by Christian Berner. The values referred to above are suitably determined by measuring the conductivity of the cellulosic suspension that is fed into or present in the headbox of the paper machine or, alternatively, by 25 measuring the conductivity of white water obtained by dewatering the suspension. High conductivity levels mean high contents of salts (electrolytes), where the various salts can be based on mono-, di- and multivalent cations like alkali metals, e.g. Na⁺ and K⁺, alkaline earths, e.g. Ca²⁺ and Mg²⁺, aluminium ions, e.g. Al³⁺, Al(OH)²⁺ and polyaluminium ions, and mono-, di- and multivalent anions like halides, e.g., Cl⁻, sulfates, e.g. SO₄²⁻ and HSO₄⁻, 30 carbonates, e.g. CO₃²⁻ and HCO₃⁻, silicates and lower organic acids. The invention is particularly useful in the manufacture of paper from stocks having high contents of salts of di- and multivalent cations, and usually the cation content is at least 200 ppm, suitably at least 300 ppm and preferably at least 400 ppm. The salts can be derived from the cellulosic fibres and fillers used to form the stock, in particular in integrated mills where a 35 concentrated aqueous fibre suspension from the pulp mill normally is mixed with water to form a dilute suspension suitable for paper manufacture in the paper mill. The salt may also

be derived from various additives introduced into the stock, from the fresh water supplied to the process, or be added deliberately, etc. Further, the content of salts is usually higher in processes where white water is extensively recirculated, which may lead to considerable accumulation of salts in the water circulating in the process.

- 5 The present invention further encompasses papermaking processes where white water is extensively recirculated (recycled), i.e. with a high degree of white water closure, for example where from 0 to 30 tons of fresh water are used per ton of dry paper produced, usually less than 20, suitably less than 15, preferably less than 10 and notably less than 5 tons of fresh water per ton of paper. Recirculation of white water obtained in the process
- 10 suitably comprises mixing the white water with cellulosic fibres and/or optional fillers to form a suspension to be dewatered; preferably it comprises mixing the white water with a suspension containing cellulosic fibres, and optional fillers, before the suspension enters the forming wire for dewatering. The white water can be mixed with the suspension before, between simultaneous with or after introducing the drainage and retention aids, if used; and
- 15 before, simultaneous with or after introducing the polysaccharide. Fresh water can be introduced in the process at any stage; for example, it can be mixed with cellulosic fibres in order to form a suspension, and it can be mixed with a suspension containing cellulosic fibres to dilute it so as to form the suspension to be dewatered, before or after mixing the stock with white water and before, between, simultaneous with or after introducing the
- 20 components of drainage and retention aids, if used; and before, simultaneous with or after introducing the polysaccharide.

Further additives which are conventional in papermaking can of course be used in combination with the additives according to the invention, such as, for example, additional dry strength agents, wet strength agents, sizing agents, e.g. those based on rosin, ketene dimers and acid anhydrides, optical brightening agents, dyes, etc. The cellulosic suspension, or stock, can also contain mineral fillers of conventional types such as, for example, kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate.

- The process of this invention is used for the production of paper. The term "paper", as used herein, of course include not only paper and the production thereof, but also other sheet or web-like products, such as for example board and paperboard, and the production thereof. The process can be used in the production of paper from different types of suspensions of cellulose-containing fibres and the suspensions should suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on dry substance. The suspensions can be based on fibres from chemical pulp such as sulphate, sulphite and organosolv pulps, mechanical pulp such as thermomechanical pulp, chemo-

thermomechanical pulp, refiner pulp and groundwood pulp, from both hardwood and softwood, and can also be based on recycled fibres, optionally from de-linked pulps, and mixtures thereof. The invention is particularly useful in the manufacture of paper from suspensions based on pulps comprising recycled fibres and de-linked pulp, and the content 5 of cellulosic fibres of such origin can be up to 100%, suitably from 20 to 100%.

The invention is further illustrated in the following Examples which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

10

Example 1

Cationised polysaccharides were prepared by reacting native potato starch with a quaternising agent according to the general procedure described in European Patent Application No. 189 935. The quaternising agents are commercially available from for example Degussa, or were prepared according to the general procedure described in 15 U.S. Patent No. 5,463,127. The starches were dissolved in water and used as 0.5% aqueous solutions.

Polysaccharides according to the invention, P1 to P3, and polysaccharides intended for comparison purposes, Ref. 1 and Ref. 2, were prepared from the following starting materials:

- 20 P1: Cationised starch obtained by quarternisation of native potato starch with 3-chloro-2-hydroxypropyl dimethyl benzyl ammonium chloride to 0.8% N.
P2: Cationised starch obtained by quarternisation of native potato starch with 3-chloro-2-hydroxypropyl dimethyl benzyl ammonium chloride to 1.3% N.
P3: Cationised starch obtained by quarternisation of native potato starch with 3-chloro-
25 2-hydroxypropyl dimethyl octyl ammonium chloride to 0.9% N.
Ref. 1: Cationised starch obtained by quarternization of native potato starch with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride to 0.8% N.
Ref. 2: Cationised starch obtained by quarternization of native potato starch with 2,3-epoxypropyl trimethyl ammonium chloride to 1.3% N.

30

Example 2

Drainage performance was evaluated by means of a Dynamic Drainage Analyser (DDA), available from Akribi, Sweden, which measures the time for draining a set volume of stock through a wire when removing a plug and applying vacuum to that 35 side of the wire opposite to the side on which the stock is present. First pass retention

was evaluated by means of a nephelometer by measuring the turbidity of the filtrate, the white water, obtained by draining the stock.

The furnish used was based on 56% by weight of peroxide bleached TMP/SGW pulp (80/20), 14% by weight of bleached birch/pine sulphate pulp (60/40) refined to 5 200° CSF and 30% by weight of china clay. To the stock was added 40 g/l of a colloidal fraction, bleach water from an SC mill, filtrated through a 5 µm screen and concentrated with an UF filter, cut off 200,000. Stock volume was 800 ml and pH about 7. Calcium chloride was added to the stock to adjust the conductivity to 5.0 mS/cm (Test Nos. 1-3), and 7.5 mS/cm (Test Nos. 4-6).

10 The stock was stirred in a baffled jar at a speed of 1500 rpm throughout the test and chemicals additions were conducted as follows: i) adding polysaccharide to the stock following by stirring for 30 seconds, ii) adding anionic inorganic particles to the stock followed by stirring for 15 seconds, iii) draining the stock while automatically recording the drainage time.

15 The polysaccharides used in the test series were P1 and Ref. 1 according to Example 1. The anionic inorganic particles used were silica-based particles of the type disclosed in U.S. Patent No. 5,368,833. The sol had an S-value of about 25% and contained silica particles with a specific surface area of about 900 m²/g which were surface-modified with aluminium to a degree of 5%.

20 Table 1 shows the dewatering and retention effect at various dosages of cationized starch, calculated as dry starch on dry stock system, and silica-based particles, calculated as SiO₂ and based on dry stock system.

Table 1

Test No.	Starch Dosage [kg/t]	SiO ₂ Dosage [kg/t]	Dewatering time [sec]		Turbidity [NTU]	
			P1	Ref. 1	P1	Ref. 1
1	7.5	3	17.0	20.6	51	61
2	10	3	16.0	20.0	54	54
3	15	3	15.0	21.0	48	52
4	7.5	1.5	18.1	22.3	53	64
5	10	1.5	16.6	22.1	55	60
6	15	1.5	15.5	24.0	50	58

In this test series, dewatering performance was evaluated according to the procedure described in Example 2.

The furnish was the same as used in Example 2. Stock volume was 800 ml and pH about 7. Calcium chloride was added to the stock to adjust the conductivity to 1.5 mS/cm (Test Nos. 1-3); 3.5 mS/cm (Test Nos. 4-5); and 5.0 mS/cm (Test Nos. 6-7).

- 5 The polysaccharides used for in the test series were P2 and Ref. 2 according to Example 1. The anionic inorganic particles according to Example 2 were similarly used in this test series.

Table 2 shows the dewatering effect at various dosages of drainage and retention aids, calculated as dry starch and SiO₂ on dry stock system.

Table 2

Test No.	Starch Dosage [kg/t]	SiO ₂ Dosage [kg/t]	Dewatering time [s]	
			P2	Ref. 2
1	0	0	22.5	22.5
2	5	3	16.3	18.0
3	10	3	10.3	10.7
4	5	3	11.6	13.4
5	10	3	9.9	10.4
6	5	3	13.1	17.9
7	10	3	10.8	15.0

10

Example 4

- In this test series, the dewatering effect was evaluated according to the procedure described in Example 2 except that the drainage and retention aids also comprised a low molecular weight cationic polyamine; ATC. The polyamine was added to 15 the stock followed by stirring for 30 seconds before addition of cationized polysaccharide and then anionic inorganic particles.

The furnish used was based on 70% deinked pulp, 15% by weight of peroxide bleached TMP/SGW pulp (80/20), and 15% by weight of bleached birch/pine sulphate pulp (60/40) refined to 200° CSF. Stock volume was 800 ml and pH about 7. Calcium 20 chloride was added to the stock to adjust the conductivity to 1.0 mS/cm (Test No. 1), 2.0 mS/cm (Test No. 2), 4.0 mS/cm (Test Nos. 3-4) and 7.5 mS/cm (Test No 5).

The polysaccharides used for in the test series were P1, P2, Ref. 1 and Ref. 2 according to Example 1. The anionic inorganic particles according to Example 2 were similarly used.

- 25 Table 3 shows the dewatering effect at various dosages of drainage and retention aids, calculated as dry polyamine, starch and SiO₂ on dry stock system.

Table 3

T st N .	ATC Dosage [kg/t]	Starch D sage [kg/t]	SiO ₂ Dosage [kg/t]	Dewatering time [s]			
				P1	P3	Ref. 1	Ref. 2
1	3	2.5	3	12.1	-	13.2	-
2	3	2.5	3	12.3	12.9	13	-
3	3	2.5	3	13.3	13.9	14.5	-
4	3	5	3	11.6	12.8	13	-
5	3	7.5	3	-	13.8	-	16

Example 5

Dry strength performance was evaluated with a Dynamic Sheet Former (Formette Dynamique), supplied by Fibertech AB, Sweden, and a Tensile Strength Tester supplied by Lorentzen & Wettre, Sweden. Dewatering effect was evaluated according to the procedure described in Example 4.

The furnish according to Example 2 was used. Stock consistency was 0.3%. Conductivity of the stock was adjusted by addition of calcium chloride. Additives and order of addition according to Example 4 were used in this test series. The polyamine was added in an amount of 3 kg/ton, calculated as dry polyamine on dry stock system. The silica-based particles were added in an amount of 3 kg/ton, calculated as SiO₂ and based on dry stock system.

Paper sheets were formed in the Dynamic Sheet Former by adding the chemicals to the stock in the mixing chest, pumping the stock through a traversing nozzle into the rotating drum onto the water film on top of the wire, draining the stock to form a sheet, pressing and drying the sheet. The sheets were cut into strips that were evaluated in the Tensile Strength Tester. The square mean value of the tensile strength index of the machine and cross direction of the paper sheets was calculated and compared.

Table 4 shows the dewatering time and tensile strength of the sheets obtained at various starch dosages, calculated as dry starch on dry stock system.

Table 4

Test No.	Conductivity [mS/cm]	Starch Dosage [kg/t]	Dewatering time [sec]		Tensile Strength [kNm/kg]	
			P2	Ref. 2	P2	Ref. 2
1	2.5	5.0	7.9	8.4	36.0	35.2
2	5.0	5.0	8.6	11.3	36.1	35.8
3	10.0	5.0	11.1	13.0	35.3	35.0
4	10.0	10.0	13.3	15.1	36.5	34.0

Claims

1. A process for the production of paper from a suspension containing cellulosic fibres, and optional fillers, comprising adding to the suspension a drainage and retention aid comprising a cationic or amphoteric polysaccharide, forming and dewatering the suspension on a wire, characterised in that the polysaccharide has a hydrophobic group.
- 5
2. A process for the production of paper from a suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a dry strength agent comprising a cationic or amphoteric polysaccharide, forming and dewatering the suspension on a wire, characterised in that the polysaccharide has a hydrophobic group.
- 10
3. A process according to claim 1 or 2, characterised in that the hydrophobic group contains from 4 to 14 carbon atoms.
- 15
4. A process according to claim 1, 2 or 3, characterised in that the hydrophobic group contains from 6 to 12 carbon atoms.
5. A process according to claim 1, 2, 3 or 4, characterised in that the hydrophobic group is attached to a charged nitrogen which in turn is attached to the polysaccharide backbone via a chain of atoms.
- 20
6. A process according to any of the preceding claims, characterised in that the hydrophobic group comprises an aromatic group.
7. A process according to any of the preceding claims, characterised in that the hydrophobic group comprises an alkyl group.
- 25
8. A process according to any of the preceding claims, characterised in that the polysaccharide is selected from starches and guar gums.
9. A process according to any of the preceding claims, characterised in that the polysaccharide contains one or more quaternary ammonium groups.
- 20
10. A process according to any of the preceding claims, characterised in that the polysaccharide contains one or more anionic groups.
11. A process according to any of the preceding claims, characterised in that the drainage and retention aid further comprises an anionic microparticulate material.
- 30
12. A process according to claim 11, characterised in that the anionic microparticulate material is selected from silica-based particles or bentonite.
13. A process according to claim 11 or 12, characterised in that the anionic microparticulate material is selected from silica-based particles having a specific surface area above 50 m²/g.
- 35

14. A process according to any of the preceding claims, characterised in that the drainage and retention aid further comprises a low molecular weight cationic organic polymer.

15. A process according to any of the preceding claims, characterised in
5 that the suspension comprises recycled cellulosic fibres.

16. A process according to any of the preceding claims, characterised in that the suspension comprises de-inked pulp.

17. A process according to any of the preceding claims, characterised in
that the suspension that is dewatered on the wire has a conductivity of at least 0.75
10 mS/cm.

18. A process according to claim 17, characterised in that the suspension that is dewatered on the wire has a conductivity of at least 2.0 mS/cm.

19. A process according to any of the preceding claims, characterised in
that the process further comprises dewatering the suspension on a wire to obtain a wet
15 web of paper and white water, recirculating the white water and optionally introducing fresh
water to form a suspension containing cellulosic fibres, and optional fillers, to be dewatered,
wherein the amount of fresh water introduced is less than 30 tons per ton of dry paper
produced.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/SE 99/00679

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H23/04 //D21H17:24, D21H21:10, D21H21:18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 388 150 A (SUNDEN OLOF ET AL) 14 June 1983 (1983-06-14) cited in the application abstract; claim 1 column 14, line 3 - line 14 ---	1-19
Y	US 4 687 519 A (TRZASKO PETER T ET AL) 18 August 1987 (1987-08-18) cited in the application column 4, line 46 -column 5, line 38 ---	1-19
A	EP 0 335 575 A (ALLIED COLLOIDS LTD) 4 October 1989 (1989-10-04) page 3, line 49 - line 55 page 4, line 22 - line 23 ---	1,2 -/-



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/SE 99/00679

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 098 520 A (NALCO CHEMICAL CO) 24 March 1992 (1992-03-24) the whole document ---	1,2
A	EP 0 752 496 A (EKA CHEMICALS AB) 8 January 1997 (1997-01-08) ---	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr	nal Application No
PCT/SE 99/00679	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4388150	A 14-06-1983	SE 432951 B AR 231848 A AT 8916 T AU 546999 B AU 7051481 A BR 8103345 A CA 1154563 A EP 0041056 A ES 502531 A FI 811628 A, B, JP 1679274 C JP 3041598 B JP 62223395 A JP 1713993 C JP 57051900 A JP 62031120 B NZ 197223 A SE 8003948 A SU 1228793 A		30-04-1984 29-03-1985 15-08-1984 03-10-1985 03-12-1981 16-02-1982 04-10-1983 02-12-1981 16-02-1983 29-11-1981 13-07-1992 24-06-1991 01-10-1987 27-11-1992 26-03-1982 07-07-1987 31-05-1984 29-11-1981 30-04-1986
US 4687519	A 18-08-1987	CA 1284562 A EP 0228576 A FI 865243 A, B, JP 62156394 A US 4721655 A		04-06-1991 15-07-1987 21-06-1987 11-07-1987 26-01-1988
EP 0335575	A 04-10-1989	AT 86693 T AU 3174989 A CA 1322435 A DE 68905208 T ES 2053980 T FI 891465 A, B, JP 2006683 A JP 5029719 B JP 5239800 A KR 9602733 B NO 174724 B US 4913775 A		15-03-1993 28-09-1989 28-09-1993 07-10-1993 01-08-1994 29-09-1989 10-01-1990 06-05-1993 17-09-1993 26-02-1996 14-03-1994 03-04-1990
US 5098520	A 24-03-1992	AT 114178 T AU 656541 B AU 8831991 A DE 69105193 D DE 69105193 T DK 497030 T EP 0497030 A ES 2067155 T FI 913469 A, B, GR 3014980 T JP 2831165 B JP 4245998 A NO 177394 B US 5185062 A		15-12-1994 09-02-1995 30-07-1992 22-12-1994 18-05-1995 18-04-1995 05-08-1992 16-03-1995 26-07-1992 31-05-1995 02-12-1998 02-09-1992 29-05-1995 09-02-1993
EP 0752496	A 08-01-1997	AU 691428 B AU 5830096 A BR 9602943 A CA 2180404 A		14-05-1998 23-01-1997 28-04-1998 08-01-1997

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/SE 99/00679

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0752496 A		CN 1145967 A	26-03-1997
		JP 9031885 A	04-02-1997
		NO 962845 A	08-01-1997
		NZ 286923 A	22-09-1997
		PL 315106 A	20-01-1997
		US 5858174 A	12-01-1999